

PAPER • OPEN ACCESS

Synthesis of α -Al₂O₃ coatings by reactive anodic arc evaporation under high-density low-energy ion assistance

To cite this article: N V Gavrilov *et al* 2019 *J. Phys.: Conf. Ser.* **1281** 012020

View the [article online](#) for updates and enhancements.



IOP | ebooks™

Bringing together innovative digital publishing with leading authors from the global scientific community.

Start exploring the collection—download the first chapter of every title for free.

Synthesis of α -Al₂O₃ coatings by reactive anodic arc evaporation under high-density low-energy ion assistance

N V Gavrilov¹, A S Kamenetskikh^{1,2}, P V Tretnikov¹ and A V Chukin²

¹Institute of Electrophysics, 620016, 106 Amundsen str., Yekaterinburg, Russia

²Ural Federal University, 620002, 19 Mira str., 620002 Yekaterinburg, Russia

E-mail: alx@iep.uran.ru

Abstract. Reactive anode evaporation of Al on metallic substrates with an isostructural sublayer at a temperature of 640 °C has allowed obtaining α -Al₂O₃ coating at a rate of 4.5 $\mu\text{m/h}$. It has been shown that the use of low-energy (50 eV) intense (up to 15 mA/cm²) ion assistance with a low content of metal ions ensures the formation of the Al₂O₃ α -phase with a low level of micro-distortions (less than 0.15%), an increased nanocrystallite size (more than 40 nm) and low internal stress (up to 2 GPa).

1. Introduction

High mechanical properties and chemical inertness at high temperatures allow using α -Al₂O₃ as a material for wear resistant and thermal barrier coating [1], but the widespread use of such coatings is limited due to the high temperature of thermally activated α -phase crystallization (~1050 °C). The application of plasma-assisted CVD has allowed reducing the temperature of α -Al₂O₃ coating synthesis to 580 °C [2]. PVD methods for low-temperature α -Al₂O₃ synthesis are developed through the intensification of surface migration of the deposited atoms by intense ion bombardment [3, 4]. For these purposes, the cathode arc with filtered plasma [5] and pulsed magnetron discharge [6, 7] are most frequently used.

The influence of deposition temperature on the structural-phase state of Al₂O₃ coatings obtained in the pulse dual magnetron system was investigated in [6]. The transition of Al₂O₃ from the amorphous into the single γ -phase occurred in the temperature range of 480–560 °C; a single-phase α -Al₂O₃ coating was obtained at 760 °C. The application of negative bias voltage –200 V has allowed lowering the temperature of α -phase appearance to –500 °C [3]. A diagram of crystal phases illustrating the influence of substrate temperature and bias voltage on the phase structure of Al₂O₃ coating was obtained in [4]. It was found that the energy of the ions required for the formation of α -Al₂O₃ through deposition from cathodic arc plasma increases with decreasing temperature and equals to 150 eV at a substrate temperature of 700 °C. Ion bombardment increases the lattice defect and the level of micro strains, which leads to γ - α recrystallization of coatings [8]. However, the size of α -phase nanocrystallites reduces with increasing energy of ions. After reaching critical sizes (~12 nm), the γ -phase begins to dominate due to differences in surface energies of the α - and γ -phases [9]. This limits the possibility of lowering synthesis temperature for α -Al₂O₃ coatings by recrystallization of the γ -phase under the influence of bombardment by ions with energy more than ~100 eV.

The use of a crystallographic template that creates conditions for the local epitaxial growth of the α -phase allows avoiding problems of competition between the α - and γ -phases at the initial stage of coating growth [10]. However, this method also has restrictions on the ion exposure intensity, and



therefore the deposition rate, because the increased energy of ions causes amorphisation of the isostructural sub-layer. This promotes the growth of the γ -phase and reducing the energy of bombarding ions leads to a decrease in the rate of migration of adsorbed atoms.

Modeling of the growth of α -Al₂O₃ coatings using the molecular dynamics method has shown the existence of a specific range of energy values for ions (Al⁺, 50–70 eV), in which α -Al₂O₃ steadily grows [11]. The appearance of even a small percentage of high-energy aluminium ions disrupts the conditions of α -phase growth. However, for ions that do not belong to the coating (Ar⁺), the threshold of destructive energy impact turned out to be significantly higher (~200 eV) than for metal ions.

This conclusion was experimentally confirmed in the study of deposition of α -Al₂O₃ coatings using anodic evaporation in an arc with self-heating cathode. The evaporation mode with a low degree of ionization of metallic vapor using the crystallographic sublayer allowed implementing the local epitaxial growth of α -Al₂O₃ [12]. The coating consisting of a mixture of α and γ -Al₂O₃ deposited under a high degree of ionization of metallic vapor (~0.8). The content of α -Al₂O₃ close to 100% was obtained only at high ion energy (200 eV) [13]. In such condition, despite the existence of the Cr₂O₃ sublayer, the γ -phase is formed at initial stages. This phase subsequently transforms into α -Al₂O₃ at a certain coating thickness largely dependent on the ion energy.

Thus, the reduction of concentration of aluminum ions in the plasma and the restriction of ion energy are necessary for the realization of the low-temperature high-speed synthesis of α -Al₂O₃ coatings on the crystallographic template. The additional supply of energy to the growing coating surface can be provided in this case by increasing the density of ion current. This work presents the study of the structure and properties of Al₂O₃ coatings obtained through reactive anode evaporation in an arc with a self-heating hollow cathode using the Cr₂O₃ sublayer at reduced (50 eV) ion energy and ion current density up to 15 mA/cm². The work contains the results of analysis of the phase composition and microstructure of coatings, the level of micro strains and intrinsic stresses through XRD and SEM methods, and also measures the growth rate, thickness, and microhardness of coatings.

2. Experimental technique

Evaporation of aluminum and deposition of coatings occurs in the discharge plasma with a self-heating hollow cathode 1, a thermally insulated graphite anode-crucible 2 and a water-cooled hollow anode 3 with an input aperture 1 cm² (figure 1). The cathode is placed inside the solenoid 4. The sample holder 5 is installed at a distance of 100 mm from the crucible. The temperature of the samples (640 °C) is adjusted by the heater 6. A discharge with a current of up to 40 A burns in a stream of argon (30-60 sccm). Oxygen flow supplied through the hollow anode is adjusted within 30-90 sccm. Part of the discharge current (3.5 A) is closed on the anode-crucible; hollow anode current changed within 8-36 A. Pulse bias voltage (0-200 V, 50 kHz, 10 μ s) was supplied to the sample holder. The coating was deposited onto the stainless steel substrate with a Cr₂O₃ sublayer with a thickness of 0.1 μ m. The vacuum chamber was pumped by a turbomolecular pump, the residual pressure was 10⁻³ Pa, the operating pressure of the Ar+O₂ mixture was ~0.1 Pa. The surface temperature of coatings was measured using a pyrometer Optris CTfast operating in a temperature range of 50-975 °C with a resolution of 0.4 °C.

The microhardness of coatings was determined using an ultramicrohardness tester DUH-211/211S, coating thickness was measured on a Calotest device, x-ray diffraction analysis was performed using diffractometer XRD-7000. The structure of films in cross-section and on the surface of coatings was studied on a raster electronic microscope LEO 982.

3. Results

An increase in the density of ion current from the plasma was achieved through an increase in the current of the hollow anode circuit and the application of the solenoid magnetic field. Ion current almost linearly increases with anode current; the use of magnetic coils with a maximum current 19 A increases current density by 2-3 mA/cm² (figure 2). Figure 3 shows diffraction patterns of Al₂O₃ coatings obtained with different density of ion current on samples.

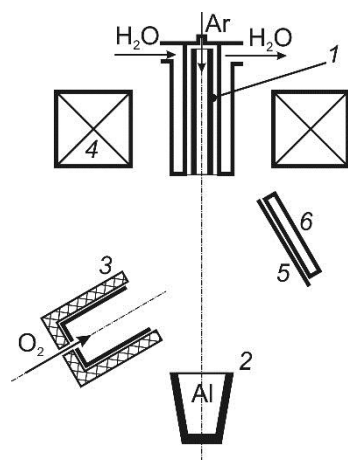


Figure 1. Experimental facility. 1 – self-heating cathode, 2 – anode-crucible, 3 – hollow anode, 4 – magnetic coil, 5 – samples, 6 – heater.

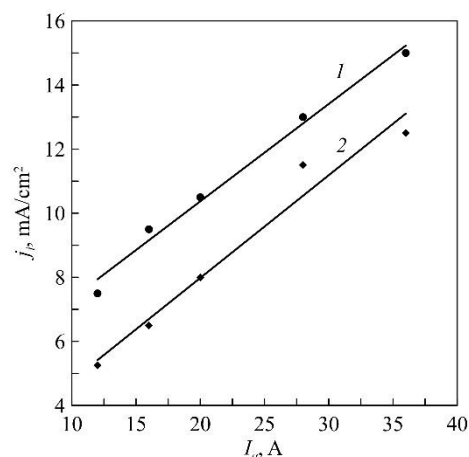


Figure 2. Ion current density vs anode current. Magnetic coil current: 1 – 19 A, 2 – 0.

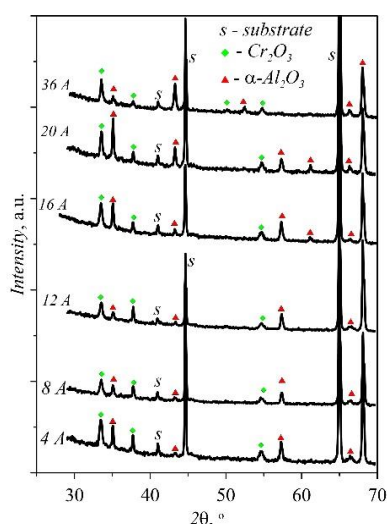


Figure 3. XRD patterns of Al_2O_3 coatings deposited under different values of the anode current.

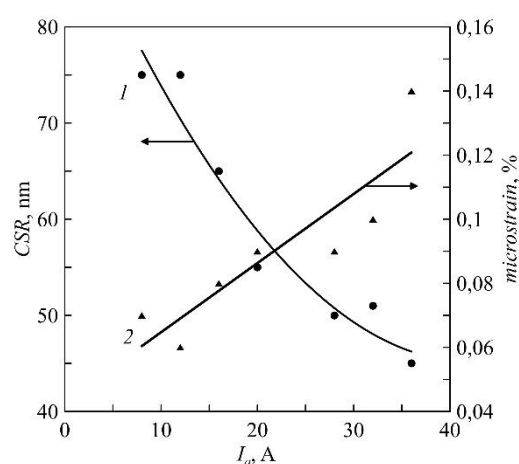


Figure 4. CSR (1) and micro strain (2) vs anode current.

The dominant phase in the coating is $\alpha\text{-Al}_2\text{O}_3$ with primary orientation (300) ($2\theta \sim 68.1^\circ$). A feature of coatings obtained at a low energy of ions is the low level of micro strains and increased size of α -phase CSR (figure 4). Intrinsic compression stress in the coatings, calculated as $\sigma = (E/2\mu)\Delta d/d$ (where μ is Poisson's ratio, $\Delta d/d$ – lattice micro strain) [14], accounted for 1.5–2 GPa, which is significantly less than 21–23 GPa for $\alpha\text{-Al}_2\text{O}_3$ coatings obtained in [6]. $\alpha\text{-Al}_2\text{O}_3$ coatings with lower intrinsic stress 3 GPa were obtained in [7], but the coating thickness was 70 nm.

Along with $\alpha\text{-Al}_2\text{O}_3$ coatings, the γ -phase was also detected; its content decreases with increasing of ion current density (figure 5). Note that this dependence shows mainly the trend of γ -phase proportion change due to the significant error of the method of its determination.

Figure 6 shows SEM images of the cross-section of the coating obtained through the cleavage method. The coating has a dense column structure with a μm lateral size of columns and smooth tops, despite the presence of textures (300) usually resulting in the formation of plate-like microstructure with platelets protruding on the surface [7].

Coating hardness measured with a load 50 mN was 18–22 GPa, Young's modulus was 270–350 GPa. An increase in current in the crucible circuit up to 5 A and anode current up to 20 A within two hours allowed obtaining the α -Al₂O₃ coating with a thickness of 9 μ m and a low level of micro-distortions (0.09 %), low internal stresses (2 GPa) and high hardness (22 GPa).

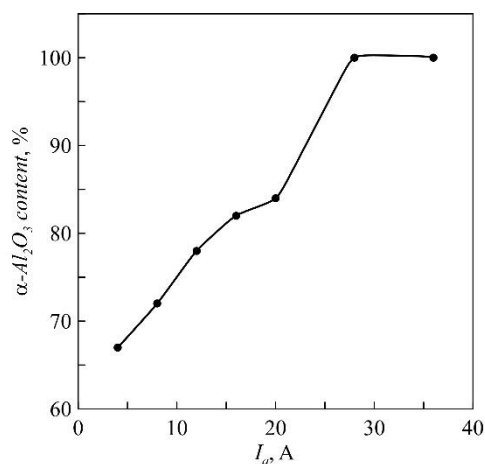


Figure 5. α -Al₂O₃ content vs anode current.

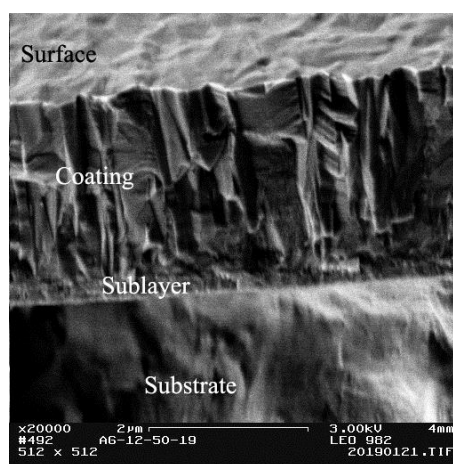


Figure 6. SEM image of the α -Al₂O₃ coating.

4. Discussion

The problem of low-temperature crystallization of the α -phase during synthesis of Al₂O₃ coatings is that the intensification of surface migration of adsorbed atoms requires additional energy supplied by ion flow. However, intensive ion bombardment results in the creation of lattice defects and growth of micro strains, as well as the reduction of the CSR, resulting in the dominance of the γ -phase in Al₂O₃.

The work devoted to the formation of nitrides TiN and TiAlN under the conditions of ion assisting highlights a significantly different impact of ion energy and ion current density on the microstructure, texture, phase composition, and nitrogen-to-metal ratio in coatings [15]. It was noted that the changes in the microstructure of coatings with increased ion current density have a close resemblance to the changes caused by rising temperatures.

It was concluded based on the results of the study of the synthesis of thin Al₂O₃ films using the technique of powerful pulsed magnetron sputtering that the approach towards low-temperature growth of α -Al₂O₃ coatings is not simply high-energy ion bombardment, but rather bombardment by ions with optimum energy and the use of sufficiently high ion fluxes [7]. This conclusion is consistent with the previously mentioned results of the modeling of the α -Al₂O₃ coating growth using the molecular dynamics method [11].

In this work, a low energy of ions (50 eV) in combination with a high density of ion current (up to 15 mA/cm²) was used, the content of aluminium ions was minimized in ion stream to the surface of the growing coating, which reduces the ion projective range and micro-distortions, as well as transfer of most of the energy of ions to adsorbed atoms and intensification of their migration across the surface.

The results obtained with high-rate deposition of Al₂O₃ coatings on the crystallographic pattern are characterized by the presence of the γ -phase in coatings and the reduction of its content with the increasing density of ion current. Diffraction patterns contain broad low-intensive lines in the areas $2\theta \sim 45.5$ and 66° , corresponding to the finely crystalline phase of Al₂O₃. Basing on the full profile Rietveld analysis [16], it was concluded that these lines belong to γ -Al₂O₃ with a grain size of 5 to 10 nm. To measure the content of the phases, the technique [17] was used, which possesses significant error (tens of %) due to the presence of substrate lines and strongly texturized phases.

Obviously, a high coating deposition rate (4.5 $\mu\text{m/h}$) does not provide conditions for local epitaxial growth of $\alpha\text{-Al}_2\text{O}_3$. The emergence of the γ -phase in the coating deposited on the crystallographic template after the reduction of the density of ion current was observed earlier in [12], the amorphous phase appeared with a significant reduction in the density of ion current along with $\gamma\text{-Al}_2\text{O}_3$.

$\alpha\text{-Al}_2\text{O}_3$ coatings obtained at 600 $^\circ\text{C}$ using the method of reactive anode evaporation followed by deposition on the crystallographic template with ion assistance in the energy range 50–200 eV with a low degree of ionization of metallic vapor was studied in [12]. A feature of these coatings obtained with an energy of ions 50 eV was low microhardness (less than 13 GPa), rapid growth of microstresses and microcrystallite size reduction with increasing density of ion current to 8 mA/cm^2 . In this work, $\alpha\text{-Al}_2\text{O}_3$ coatings with high microhardness, low microstress and internal stress levels, with a dense column structure was obtained with a high deposition rate at a slight increase in temperature up to 640 $^\circ\text{C}$ and ion current density growth over 10 mA/cm^2 .

5. Conclusion

It has been shown that the Al_2O_3 synthesis regime using the crystallographic template under the conditions of high ion current, a low (50 eV) energy of ions and a small content of aluminum ions in ion flow ensures the formation of the Al_2O_3 α -phase with a low micro-distortion level, an increased size of nanocrystallites and low internal stresses (up to 2 GPa). This mode of local epitaxial growth at a temperature of 640 $^\circ\text{C}$ allowed obtaining the $\alpha\text{-Al}_2\text{O}_3$ coating with a thickness of up to 9 μm at a rate of 4.5 $\mu\text{m/h}$. At high-speed coating deposition, the growth of density of ion assistance current leads to a reduction of the content of finely crystalline γ -phase in Al_2O_3 and ensures the formation of the single-phase $\alpha\text{-Al}_2\text{O}_3$ coating.

Acknowledgment

This work was supported by the Russian Science Foundation under grant No. 18-19-00567.

References

- [1] Ruppel S 2001 *Journal de Physique IV* **11** 847–59
- [2] Kyrylov O, Kurapov D and Schneider J M 2005 *Appl. Phys. A* **80** 1657–60
- [3] Yamada-Takamura Y, Koch F, Maier H and Bolt H 2001 *Surf. Coatings Technol.* **142–144** 260–4
- [4] Brill R, Koch F, Mazurelle J, Levchuk D, Balden M, Yamada-Takamura Y, Maier H and Bolt H 2003 *Surf. Coatings Technol.* **174–175** 606–10
- [5] Rosen J, Mraz S, Kreissig U, Music D and Schneider J M 2005 *Plasma Chemistry and Plasma Processing* **25** 303–17
- [6] Zywitzki O, Hoetzsch G, Fietzke F and Goedicke K. 1996 *Surf. Coatings Technol.* **82** 169–75
- [7] Wallin E, Selinder T I, Elfving M and Helmersson U 2008 *EPL* **82** 36002
- [8] Davis C A 1993 *Thin Solid Films* **226** 30–4
- [9] McHale J M 1997 *Science* **277** 788–91
- [10] Jin P, Xu G, Tazawa M, Yoshimura K, Music D, Alami J and Helmersson U 2002 *J. Vac. Sci. Technol. A* **20** 2134–6
- [11] Houska J 2013 *Surf. Coatings Technol.* **235** 333–41
- [12] Gavrilov N V, Kamenetskikh A S, Tretnikov P V and Chukin A V 2018 *Surf. Coatings Technol.* **337** 453–60
- [13] Gavrilov N V, Kamenetskikh A S, Tretnikov P V, Emlin D R, Chukin A V and Surkov Yu S 2019 *Surf. Coatings Technol.* **359** 117–24
- [14] Noyan I C and Cohen J B 1987 *Residual Stress. Measurement by Diffraction and Interpolation* Springer-Verlag, New York
- [15] Petrov I, Adibi F, Greene J E, Hultman L and Sundgren J E 1993 *Appl. Phys. Lett.* **63** 36–8
- [16] Rietveld H M 1969 *J. Appl. Crystallogr.* **2** 65–71
- [17] Hill R J and Howard C J 1987 *J. Appl. Crystallogr.* **20** 467–74